THERMOLYSIS OF SURFACE-ATTACHED 1,3-DIPHENYLPROPANE: IMPACT OF SURFACE IMMOBILIZATION ON THERMAL REACTION MECHANISMS

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INTRODUCTION

Attempts to understand the thermal chemistry of coal at the molecular level are severely complicated by its inherent properties: a diverse array of structural units (e.g., aromatic, hydroaromatic, and heterocyclic aromatic clusters connected by short aliphatic and ether links) and functional groups (e.g., phenolic hydroxyls, carboxyls, and basic nitrogens) in a cross-linked macromolecular framework with no repeating units (1,2). One simplifying experimental approach has been the study of individual model compounds that highlight structural features in coal. A complicating feature in the interpretive extrapolation of model compound behavior to coal is the possible modifications in free-radical reactivity patterns resulting from restricted translational mobility in the coal where breaking one bond in the macromolecular structure will result in radical centers that are still attached to the residual framework. We are modeling this phenomenon by studying the thermolysis of model compounds that are immobilized by covalent attachment to an inert surface. Previous studies of surface-immobilized bibenzyl (1,2-diphenylethane) showed that immobilization can profoundly alter free-radical reaction pathways compared with the corresponding fluid phase behavior (3). In particular, free-radical chain pathways became dominant decay routes leading to rearrangement, cyclization, and hydrogenolysis of the bibenzyl groups. In this paper we describe preliminary results on the effects of surface immobilization on the thermolysis of 1,3-diphenylpropane, whose fluid phase behavior has been extensively investigated (4-8).

EXPERIMENTAL

Surface-immobilized 1,3-diphenylpropane (~~DPP) was prepared at saturation coverage by the condensation at 225 °C of excess p-$HOPh(CH_2)_3Ph$ with the surface hydroxyl groups of a fumed silica (Cabosil M-5, Cabot Corp., 200 m^2/g) according to the procedure described previously for surface-immobilized bibenzyl (3). Excess phenol was removed by heating at 300 (Batch A) or 270 °C (Batch B) for 0.5 h under a dynamic vacuum. The lower temperature used for Batch B appears to minimize a trace amount of reaction (ca. 0.02%) that occurs during this purification stage. GC analysis following a base hydrolysis assay procedure (3) gave coverages of 0.586 (Batch A) and 0.566 (Batch B) mmol ~~DPP per gram of final product. The starting phenol was prepared by the acid catalyzed condensation of cinnamyl alcohol ($PhCH{=}CHCH_2OH$) and phenol (9) followed by catalytic hydrogenation (10% Pd/carbon) of the olefinic intermediate.

Thermolysis (in sealed, evacuated tubes) and product analysis procedures have been thoroughly described elsewhere (3). Typically 0.3-0.4 g of surface-attached material (0.17-0.23 mmol ~~DPP) are employed, and volatile products are collected in a cold trap and then analyzed by GC and GC-MS. In a separate procedure surface-attached products are liberated as phenols following digestion of the silica in 1 N NaOH, silylated to the corresponding trimethylsilyl ethers, and analyzed as above.

RESULTS AND DISCUSSION

Thermolyses have been performed at 345 and 375 °C, and the product distributions for the four major primary products and the major secondary products are shown as a function of ∼∼DPP conversion in Figure 1a. The two lowest conversion runs (1.50 and 1.94%) were obtained at 345 °C, while the remainder of the data was obtained at 375 °C. Results from the two different high coverage batches of ∼∼DPP were consistent in terms of products detected and their relative yields. The only difference observed was a slightly slower reaction rate for batch B (ca. 30%) perhaps reflecting a slightly higher purity as a result of purification at the lower temperature (see experimental section).

We find that at low conversions (<∼3%) ∼∼DPP cracks to form four major products in essentially equal amounts as shown below.

$$\sim\sim Ph(CH_2)_3Ph \rightarrow \underset{1}{\sim\sim PhCH_3} + \underset{2}{PhCH{=}CH_2} + \underset{3}{\sim\sim PhCH{=}CH_2} + \underset{4}{PhCH_3} \qquad 1)$$

Thermolysis of liquid DPP at very low conversions also gave a correspondingly simple product distribution as shown in Eq. 2 (4).

$$Ph(CH_2)_3Ph \rightarrow PhCH_3 + PhCH{=}CH_2 \qquad 2)$$

Hence at low conversions, the surface-immobilized DPP is reacting in an analogous fashion to liquid DPP. The additional product pair observed in the thermolysis of ∼∼DPP results from the fact that the two ends of the DPP molecule are no longer equivalent upon covalent surface attachment. The initial rate of the ∼∼DPP reaction is 15-20% h^{-1} at 375 °C for the two batches (based on a 2.3-3.0% conversion after a 9 min reaction period), and this decomposition rate is comparable to that measured for liquid DPP (ca. 19% h^{-1}) (4). This further indicates that surface immobilization at high coverage is not perturbing the initial reaction behavior of the DPP moiety.

The facile decomposition of liquid DPP was demonstrated to arise from a radical chain route whose chain propagation steps are shown in Eqs. 3 and 4 (4). In the case

$$Ph\dot{C}H_2 + PhCH_2CH_2CH_2Ph \rightarrow PhCH_3 + Ph\dot{C}HCH_2CH_2Ph \qquad 3)$$

$$Ph\dot{C}HCH_2CH_2Ph \rightarrow PhCH{=}CH_2 + Ph\dot{C}H_2 \qquad 4)$$

of ∼∼DPP, two distinct benzylic radicals can be formed by hydrogen abstraction (Eq. 6) following a small amount of initial homolysis (Eq. 5). Each radical can then undergo a rapid β-scission process (Eqs. 7 and 8) to produce the surface bound and free styrene products (**3** and **2** respectively) analogous to Eq. 4. The free and surface-immobilized benzyl radicals propagate the chain by reacting with ∼∼DPP (Eq. 6; R = $PhCH_2$) to form the free and surface bound toluene products (**4** and **1** respectively) while regenerating **5** and **6**.

$$\sim\sim Ph(CH_2)_3Ph \rightarrow \sim\sim Ph\dot{C}H_2 + PhCH_2\dot{C}H_2 \qquad 5a)$$

$$\sim\sim Ph(CH_2)_3Ph \rightarrow \sim\sim PhCH_2\dot{C}H_2 + Ph\dot{C}H_2 \qquad 5b)$$

$$\sim\!\sim Ph(CH_2)_3Ph + R\bullet \ (\text{or} \sim\!\sim R\bullet) \longrightarrow \underset{\mathbf{5}}{\sim\!\sim Ph\dot{C}HCH_2CH_2Ph} + RH \ (\text{or} \sim\!\sim RH) \qquad 6a)$$

$$\sim\!\sim Ph(CH_2)_3Ph + R\bullet \ (\text{or} \sim\!\sim R\bullet) \longrightarrow \underset{\mathbf{6}}{\sim\!\sim PhCH_2CH_2\dot{C}HPh} + RH \ (\text{or} \sim\!\sim RH) \qquad 6b)$$

$$\underset{\mathbf{5}}{\sim\!\sim Ph\dot{C}HCH_2CH_2Ph} \rightarrow \sim\!\sim PhCH{=}CH_2 + Ph\dot{C}H_2 \qquad 7)$$

$$\underset{\mathbf{6}}{\sim\!\sim PhCH_2CH_2\dot{C}HPh} \rightarrow \sim\!\sim Ph\dot{C}H_2 + PhCH{=}CH_2 \qquad 8)$$

No selectivity is observed for the two possible decay routes that form the product pairs 1 and 2 or 3 and 4. This suggests that at low conversions, radicals 5 and 6 are formed with equal probability and that their β-scission reactions (Eqs. 7 and 8) occur at equal rates. Trace quantities of other primary products (each <0.05 mol% of the products) including free and surface bound PhC_2H_5 (Eq. 6; R = PhC_2H_4) and free bibenzyl (from benzyl radical coupling) are also detected.

As the conversion of ~~DPP increases, there is a divergence in the yields of the four main products (Fig. 1a), and several secondary products are formed in small but increasing yields. The most significant of these (reaching about 2.8 mol % of the products at 23% conversion) is ~~$Ph(CH_2)_3Ph$~~, 7 (identified by GC-MS as the corresponding bistrimethylsilyl ether after workup). The formation of this doubly attached product arises from a secondary reaction that consumes 3, perhaps via addition of surface-attached benzyl radical (which would normally have reacted to form 1) to the surface-attached styrene. Additional secondary products observed at higher conversion include several unidentified isomers of composition corresponding to ~~$C_{23}H_{22}$~~. These products also involve the consumption of surface bound styrene (and a ~~DPP) and have a formal analog, 1,3,5-triphenylpentane, amongst the secondary products detected in the thermolysis of liquid DPP (4). However even at the highest conversion studied (23%), the secondary products sum to only 5 mol % of the total products. The radical chain decomposition of surface-immobilized DPP is a very efficient process with an estimated kinetic chain length (c.l.≡ (PhVi + ~~PhVi)/4PhEt) of 200 at 345 °C. This calculation assumes that there is no selectivity in the initial homolysis (Eq. 5) and that all $PhC_2H_4\bullet$ start chains.

One of the most interesting features to emerge from this study is an observed selectivity for the radical chain reaction path that forms 1 and 2 relative to that which forms 3 and 4 as the conversion increases. This is most clearly seen in Fig. 1b where the styrene to toluene yield ratio (these products are not consumed in secondary reactions) is used as an indicator of this selectivity. The ratio increases monotonically from a value of 1.00 (±0.02) indicating no selectivity at conversions <4% to a value of 1.41 (±0.04) at 23% conversion. We previously observed in the case of surface-immobilized bibenzyl that reaction rates of radical chain pathways are very sensitive to changes in surface coverage (3). These studies also indicated that unimolecular steps such as Eqs. 7 and 8 should be unaffected by such surface coverage changes. The observed regiospecificity in the reaction of ~~DPP at higher conversions may indicate that, as the molecules of ~~DPP become spread apart on the surface, hydrogen abstraction at the benzylic carbon that is farthest from the surface is becoming favored, i.e., selectivity for formation of 6 (Eq. 6b) relative to 5 (Eq. 6a). However the complication resulting from the formation of secondary products, which likely involve the reaction of 5 and 6, does not allow a firm conclusion to be reached at this time. Additional insights into the cause of this regiospecificity should be gained from current studies being performed at lower initial surface coverages.

CONCLUSIONS

Covalent attachment of organic compounds onto an inert silica surface has proven to be a successful methodology for exploring the thermal reaction chemistry of coal model compounds under surface-immobilized conditions at temperatures relevant for coal thermolysis. Previous studies of surface-attached bibenzyl showed that restrictions on free-radical mobility can have a significant impact on reaction rates and on the nature and composition of the reaction products when compared with fluid phase behavior. The current investigation of the thermolysis of surface-immobilized 1,3-diphenylpropane has shown that facile decomposition of the trimethylene link by means of a radical chain process can still occur under surface-immobilized conditions. For ~~DPP no selectivity is observed at low conversions for the two competing radical chain decay pathways that cycle through benzylic radicals **5** and **6**. However at higher conversions, a selectivity is observed favoring the radical chain route cycling through **6**. Experiments are in progress to determine if this selectivity is a result of regiospecific hydrogen transfer on the surface at lower surface coverages.

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Figure 1. Thermolysis of ~~Ph(CH2)3Ph